

# Leaching behaviour of electrode materials of spent nickel–cadmium batteries in sulphuric acid media

C.A. Nogueira<sup>a,\*</sup>, F. Margarido<sup>b,1</sup>

<sup>a</sup>*Instituto Nacional de Engenharia e Tecnologia Industrial (INETI), Estrada do Paço Lumiar, 1649-038 Lisboa, Portugal*

<sup>b</sup>*CVRM/Geosystems Center; Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal*

Received 28 November 2002; received in revised form 6 May 2003; accepted 31 May 2003

## Abstract

The improving awareness of environmental problems associated with the toxicity of heavy metals keeps the recycling of spent nickel–cadmium batteries an important assignment due to the presence of cadmium, nickel and cobalt on the electrode material. While cadmium from batteries is one of the major sources of cadmium contamination of the environment, the other heavy metals contained on the electrode material have a considerable economic value. Therefore a complete and valorising solution to the management of this type of residues is not possible through the existing pyrometallurgical processes because the treatment of complex materials in order to recycle all materials is difficult. An integrated process based on physical and hydroelectrometallurgical operations seems to be more efficient because it is possible to recover the three metals, Cd, Ni and Co, present on the electrode material. The study here presented deals with the first chemical stage of an integrated process, the leaching of spent nickel–cadmium electrodes with sulphuric acid. The electrode materials essentially composed of Ni, Cd and Co hydroxides were readily solubilised in 0.5 h with low acid concentrations (pH ~ 1) at ambient temperature. At higher pH values the solubilisation of metal hydroxides was inefficient, except when using long residence times. The leaching of nickel present in the metallic form, in the electrodes, was more difficult due to kinetic constraints, applying high temperature (e.g. 95 °C) and acid concentration (e.g. 2.5 M H<sub>2</sub>SO<sub>4</sub>) in order to obtain complete conversions in acceptable time (~ 4 h).

© 2003 Elsevier B.V. All rights reserved.

**Keywords:** Ni–Cd batteries; Recycling; Leaching; Nickel; Cadmium; Cobalt

## 1. Introduction

The recycling of spent nickel–cadmium (Ni–Cd) batteries is currently done in Europe (Linck, 1998; Bärning, 1979, 1983), America (Hanewald, 1998) and

Japan (Ohira, 1986) using essentially pyrometallurgical processes. These processes allow the distillation of metals having a low boiling point, mainly cadmium, which is further recovered in metallic or oxide forms depending on different types of furnace technology employed, while nickel remains in the final scrap. Cobalt, which is a minor element present in the cathode, is not valorised despite its high commercial value.

Recycling processes must be as simple and inexpensive as possible. Pyrometallurgical processes are

\* Corresponding author. Tel.: +351-21-7165141; fax: +351-21-7166568.

E-mail addresses: [carlos.nogueira@ineti.pt](mailto:carlos.nogueira@ineti.pt) (C.A. Nogueira), [fernanda.margarido@ist.utl.pt](mailto:fernanda.margarido@ist.utl.pt) (F. Margarido).

<sup>1</sup> Tel.: +351-21-8418107; fax: +351-21-8418132.

relatively simple but they are not versatile, and are high energy-consumers, when compared with hydrometallurgical process. The integrated physical–hydrometallurgical processing seems to be an adequate alternative to increase treatment capacity of Ni–Cd wastes (Pons et al., 1997; Cavallini et al., 2000; Sohn et al., 2000; Espinosa and Tenorio, 2001). This approach presents several advantages over pyrometallurgical treatment, namely: (1) allows the treatment of similar nickel-bearing wastes, such as sludges, dusts and spent catalysts; (2) decreases energy consumption; (3) avoids cadmium release to the atmosphere and the subsequent environmental and health damage; (4) leads to a better valorisation of contained materials allowing the production of high purity metals or metallic compounds, and (5) is suitable to small industrial applications.

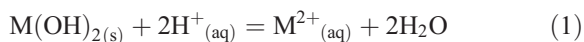
Therefore the hydrometallurgical processes to be applied shall take this into consideration, avoiding the use of expensive reagents and complex technologies. The leaching operation with sulphuric acid studied in the integrated process developed by our team (Pons et al., 1997) seems to be appropriate to accomplish these goals, providing an integrated solution for the efficient recovery of metals from the battery electrodes. The subsequent separation of metal ions is carried out by solvent extraction (Nogueira and Delmas, 1999) allowing the recovery of Ni, Cd and Co as metals by electrowinning or as salts by crystallisation.

This paper will focus on the leaching operation, comparing predicted and experimental values obtained. The relationship between the leaching efficiency and the electrode materials composition is determined by analysing the behaviour of the solid phases of the electrodes in dilute and concentrated sulphuric acid solutions. Therefore the feasibility of the hydrometallurgical processing can be assessed.

## 2. Chemistry of the solution and theoretical behaviour of phases

The hydrometallurgical processing of Ni–Cd battery wastes deals with the solubilisation of Ni, Cd and Co hydroxides, present in the active electrode materials, as well as a finely divided nickel mesh mixed with the electrodes. The behaviour of these solid phases

under acid leaching conditions can be predicted from equilibrium data. In order to simplify the calculations, molar metal ion concentrations can be used instead of activities in all formulations presented. The leaching of the metal hydroxides,  $M(OH)_2$ , where  $M = Ni, Cd$  or  $Co$ , can be summarised by the following equilibrium reaction,



represented by the respective constant  $K_1$ ,  $K_1 = [M^{2+}]/[H^+]^2$ .

According to the definition of the solubility product,  $K_S$ , for the ionic solid  $M(OH)_2$ ,  $K_S = [M^{2+}][OH^-]^2 = [M^{2+}]K_W^2/[H^+]^2$ . Therefore, the relationship  $K_1 = K_S/K_W^2$  becomes clear and it can be written as,

$$[M^{2+}]/[H^+]^2 = K_S/K_W^2 \quad (2)$$

Thus the concentration of the metal ion  $M^{2+}$  in solution, at 25 °C, can be predicted by,

$$[M^{2+}] = K_S/(10^{2pH-28}) \quad (3)$$

the Ni, Cd and Co hydroxides solubility products being obtained from thermodynamic data (Pourbaix, 1974). As demonstrated, the predicted equilibrium concentration of  $M^{2+}$  resulting from the leaching reaction depends on the equilibrium solubility constant of the metal hydroxide. This is due to the particular fact that as the reaction occurs in the aqueous phase the anion of the ionic solid ( $OH^-$ ) has with the leaching agent ( $H^+$ ) a defined and interdependent relationship. The utilisation of the above methodology should take into consideration the threshold  $M^{2+}$  concentrations given by the solubility of the metal sulphates (which are above 100 g/L of  $M^{2+}$  for the three metals involved). Considering the conditions used in the experiments ( $L/S = 20$  L/kg) and taking into consideration the composition of the electrodes, the metal concentrations attained in solution will be far from those limits, so the crystallisation of  $MSO_4$  species does not need to be considered.

The predicted concentrations for the three metals considered as a function of pH are shown in Fig. 1. As observed, Ni, Cd and Co hydroxides are very soluble in low acid concentrations. For pH values lower than 6–6.5, it is possible to reach high metal concentra-

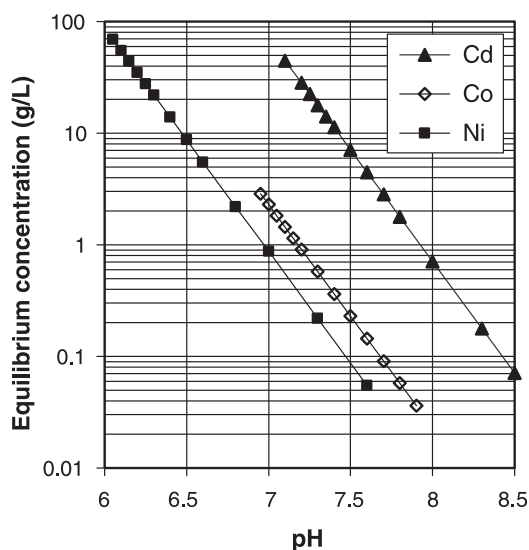
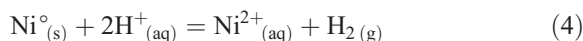


Fig. 1. Predicted concentrations of metals in solution as a function of pH, at 25 °C, from the solubility equilibrium of Ni, Cd and Co hydroxides.

tions in solution, which indicate that solubilisation conditions are adequate.

Concerning nickel species in the metallic form, during leaching experiments oxidation occurs to the divalent state, therefore the solubilisation conditions can be predicted from a potential–pH ( $E$ –pH) diagram, as represented in Fig. 2. This diagram was plotted considering two nickel ion concentrations (25 and 50 g/L) representative of the typical composition of the leaching solution in the studied process, and using thermodynamic data acquired from the literature (Pourbaix, 1974). This diagram shows that the stability region of  $\text{Ni}^{2+}$  is enclosed by the water stability limits, denoting the feasibility of nickel oxidation by the acid. For pH lower than 4.3 or 4.4 (cross points of the equilibrium lines  $\text{Ni}^0/\text{Ni}^{2+}$  and  $\text{H}_2\text{O}/\text{H}_2$  for the two  $\text{Ni}^{2+}$  concentrations), the following reaction occurs spontaneously:



The estimation of theoretical leaching yields was also carried out in defined conditions (25 °C and  $\text{L/S} = 20 \text{ L/kg}$ ) and using the above referred equilibrium data. Dissolution of metal hydroxides was estimated according to the equilibrium expression (3).

In the case of nickel, the dissolution of the metallic phase was also predicted from electrochemical data, applying the Nernst equation to the equilibrium reaction (4),

$$\log[\text{Ni}^{2+}] = \Delta E^\circ / 0.0296 - 2\text{pH} \quad (5)$$

where  $\Delta E^\circ$  is the respective standard electromotive force difference. In all cases after estimating the equilibrium concentrations as a function of pH, leaching yields for each metal,  $\eta_{\text{M}}$  (Eq. (6)), were deduced considering the initial solid composition,

$$\eta_{\text{M}} (\%) = 100[\text{M}^{2+}]\text{L}/\text{SM}_{\text{W}}/x_{\text{W}} \quad (6)$$

where  $\text{L/S}$  represents the liquid/solid ratio (volume/weight units),  $M_{\text{W}}$  the molar mass of the species and  $x_{\text{W}}$  the respective weight fraction in the initial solid material. Results obtained are represented in Fig. 3. In the case of nickel, the concentrations in solution due to the leaching of  $\text{Ni}(\text{OH})_2$  and  $\text{Ni}^0$  were obtained separately since it was expected that the leaching of these species occurs sequentially at different acidity levels. The overall Ni leaching efficiency was accomplished considering that 33% of the total nickel was present in the hydroxide form and 67%

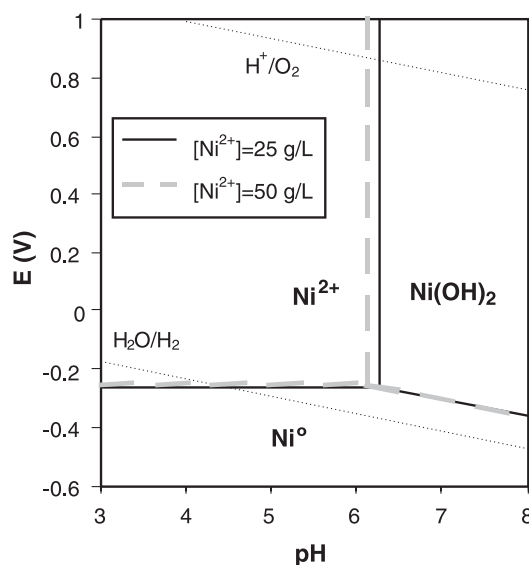


Fig. 2.  $E$ –pH diagram at 25 °C for the system  $\text{Ni}$ – $\text{H}_2\text{O}$ . Potentials are referred to standard hydrogen electrode.

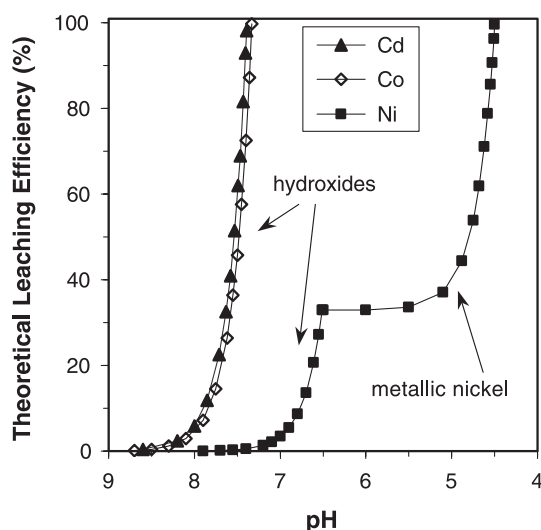


Fig. 3. Simulation of the leaching yields of the three metals present in the electrodes as a function of pH, at 25 °C and L/S=20 L/kg.

in the metallic form, as will be later experimentally justified.

### 3. Experimental

#### 3.1. Materials characterisation

Spent Ni–Cd batteries (D or Mono type) from military applications, donated by the Portuguese Army, were dismantled in order to obtain the electrode materials for the leaching tests. The iron case was open by using a lathe, the electrode plates, cathodic and anodic were carefully withdrawn and the polyamide separator removed. The electrodes were then disaggregated from the steel support plaques by twisting them, the released material being collected for the leaching experiments.

Chemical composition of the solids (the initial electrode material and the final leaching residues) was determined by atomic absorption spectrometry (GBC 906AA) after appropriate solubilisation in a mixture 1:1 (v/v) of 65% HNO<sub>3</sub> and 37% HCl, p.a. from Riedel-de Haën. The main chemical elements of electrode material are nickel and cadmium as seen in Table 1, cobalt being a minor element used as additive in the cathodic material.

Phase composition of the initial electrode material and the final leaching residues was identified by X-ray diffraction (XRD), the patterns being obtained with a Rigaku Geislerflex D/MAX III-C diffractometer (Cu K $\alpha$  radiation), equipped with a curved crystal graphite monochromator and the following conditions, 45 kV, 20 mA and a scan speed 2°(2 $\theta$ ) min<sup>-1</sup>.

Electrodes are composed of solid particles essentially made of Ni(OH)<sub>2</sub> and Cd(OH)<sub>2</sub> powders (Fig. 4a), which constitute the active cell materials, both hydroxides being mixed within a finely divided metallic nickel mesh. This metal is employed in the electrodes to allow conductivity and to improve mechanical robustness. Dark particles observed on the stereoscopic micrograph represented in Fig. 5 are the cathodic material and the light-grey the anodic material. Small amounts of polyamide fibres coming from the separator were also found inside the electrodes. According to the cumulative percent curve (Fig. 6), 88% (w/w) of the material is in the granulometric range 0.30–1.4 mm, 7% is below 0.30 mm and only 5% of the material is between 1.4 and 2.0 mm.

Samples for the leaching experiments and chemical/morphological analysis consist of about 50% (w/w) of each electrode (cathode and anode), the homogenisation being attained using a rotating divider apparatus.

#### 3.2. Leaching experiments

Leaching solutions were prepared by dilution of 95–97% H<sub>2</sub>SO<sub>4</sub>, reagent grade, from Riedel-de Haën in demineralised water. Leaching experiments were performed in thermostatted closed glass reactors (1 L maximum capacity) provided with mechanical stirrer (four-blade impeller) under constant stirring (500 ± 10 min<sup>-1</sup>). A leachant volume of 500 mL was used in each experiment, the weight of solids being chosen according to the liquid/solid ratio used (L/S = 20 L/kg, usually). When the leaching solution attained the established temperature, sample material was added

Table 1  
Chemical analysis of spent Ni–Cd battery electrodes

Elemental composition (% w/w)		
Ni	Cd	Co
51	25	0.90

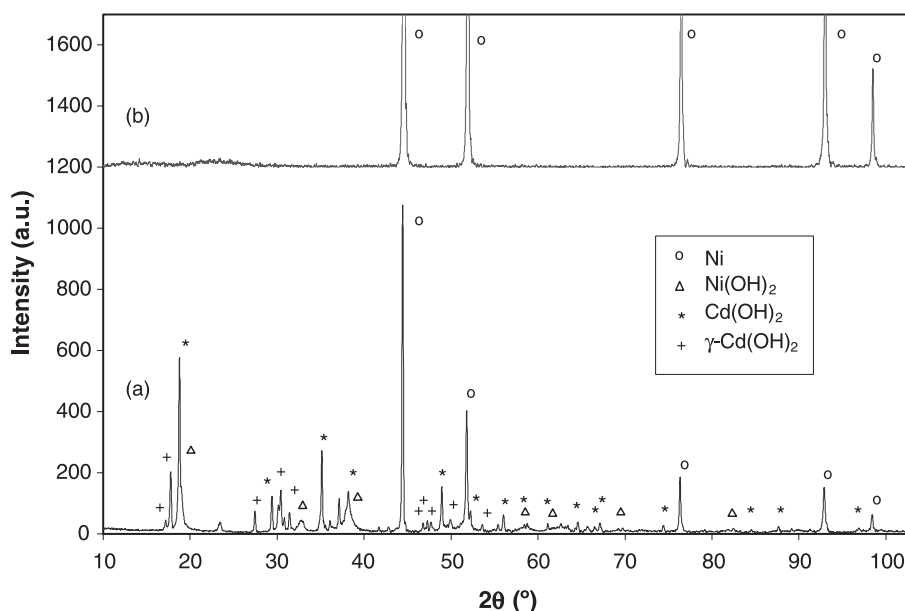


Fig. 4. XRD patterns of (a) initial electrode material, and (b) solid residue after leaching with  $\text{H}_2\text{SO}_4$  at pH 0.9, 25 °C and L/S=20 L/kg, for 30 min.

to the reactor, and the time of the experiment began at this moment.

Two series of experiments were performed according to the acid concentration, the first type being carried out with low acid concentrations at pH 0.9–4.0 and ambient temperature and the second with high acid concentrations (0.55–4 M  $\text{H}_2\text{SO}_4$ ) and moderate (50 °C) or elevated (95 °C) temperatures. Whereas the second type of reaction proceeded without any

acid compensation, in the first type of experiments, the leaching media was maintained at the preset pH value during the reaction time, by a continuous addition to the leaching reactor of a sulphuric acid solution with an accurate concentration chosen for each case, using a peristaltic pump (WM-101U/R) connected to an automatic pH controller (Eutech alpha pH-1000) for minimising volume changes. However,

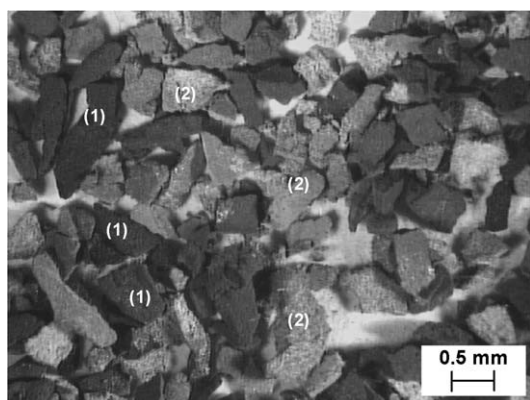


Fig. 5. General appearance of Ni–Cd battery electrode material: (1) cathodic materials; (2) anodic materials.

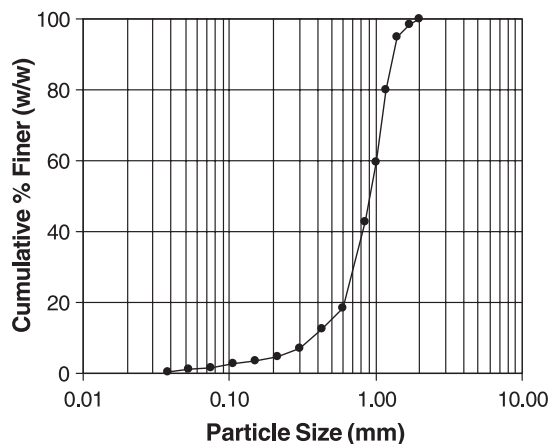


Fig. 6. Cumulative percent curve of Ni–Cd battery electrode material.

any volume variation observed during the experiments was always checked being considered in the calculation of leaching efficiencies. Liquor samples were collected for analysis using a glass tube with a cotton filter connected to a vacuum pump. Metal ion compositions in solution were determined by atomic absorption spectrometry after adequate dilution.

At the end of each experiment, the remaining solids were filtered, washed, dried and weighed for analysis. Leaching efficiencies of each metal (Ni, Cd and Co) were determined from the leach liquor composition, the final leaching yield being calculated also from the results of the solid analysis, providing comparative data for accuracy evaluation. Results obtained from liquid and solid analysis generally agree well.

#### 4. Results and discussion

Leaching efficiency data obtained by simulation and represented in Fig. 3 show that cobalt and cadmium hydroxides can be completely leached for pH values below 7.4 while the dissolution of nickel hydroxide can be achieved for pH below 6.5. Concerning metallic nickel, its solubilisation proceeds below pH = 5 being completed at pH = 4.5. From these results, it seems that, from a strictly thermodynamic point of view, the leaching of hydroxides and metallic species can be easily achieved in relatively low acid concentrations.

Experimental results of leaching efficiency for the three metals are represented in Fig. 7. On the X-axis of Fig. 7a are represented two variables: the experimental pH value and the corresponding predicted  $\text{H}_2\text{SO}_4$  concentration calculated from the acidity constants.

Cobalt and cadmium, both in hydroxide form, are completely solubilised at pH values lower than 1 (Fig. 7a). The same behaviour was observed for about 33% of the nickel present in the electrode. This value corresponds probably to the fraction of nickel in the  $\text{Ni}(\text{OH})_2$  phase, the difference (67%) being the nickel present in metallic form which was not soluble in those conditions of acidity and temperature. This hypothesis was assessed by X-ray diffraction (Fig. 4) comparing the patterns of the initial electrode material (a) and the leaching solid residues (b). In fact, XRD patterns of the initial solid and the solid

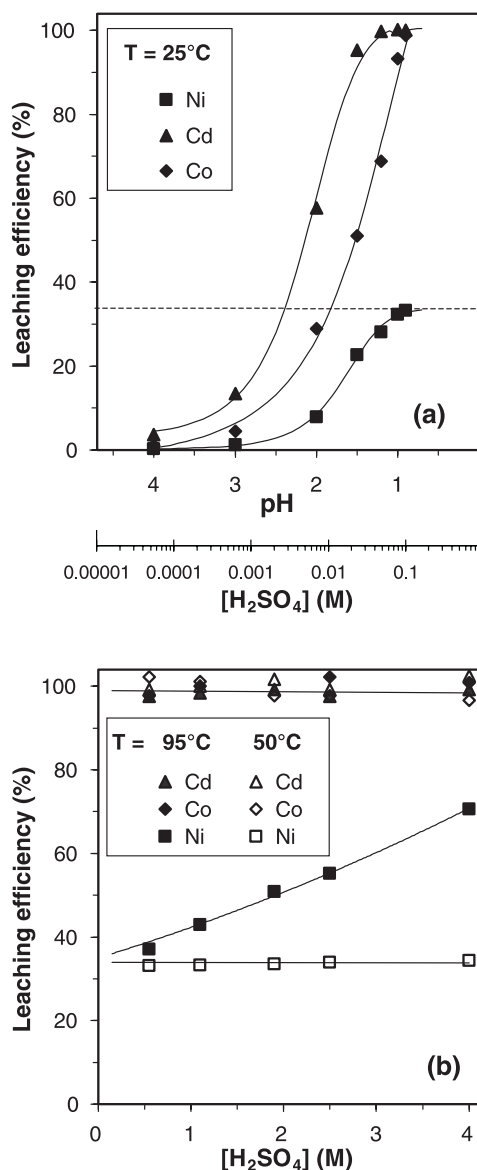


Fig. 7. Leaching efficiency of Cd, Ni and Co in several acid conditions. L/S = 20 L/kg; time = 0.5 h. (a) Weak acid conditions, at controlled pH (0.9–4) and ambient temperature; (b) high acid concentrations (0.55–4 M) and 50 or 95 °C.

residues are quite different, being visualised on the pattern (a) reflections corresponding to the Ni and Cd hydroxides and also the metallic nickel, while on pattern (b) appear only the reflections corresponding to metallic nickel.



According to the theoretical predictions (Fig. 3), higher leaching efficiencies of the hydroxides at the pH values tested would be expected. Total dissolution of these species was only achieved at pH values below 1 instead of 7.4–6.5 as theoretically foreseen. In spite of the reaction proceeding, the low driving force of the leaching agent, at those values of low acidity, caused kinetic constraints. The experimental leaching yields obtained for metallic nickel (Fig. 7a) were very different from the prediction values. For values of pH below 4.5, this species should react but, in fact, the leaching yields obtained were negligible. When high acid concentrations and moderate temperature (50 °C) were used (Fig. 7b), leaching yields of nickel were about 33–35%, which give an almost imperceptible dissolution of the metallic form. At the higher temperature (95 °C), the metallic phase reacts and the solubilisation of nickel increases with the acid concentration.

The apparent difficulty in the solubilisation of nickel can be assigned to kinetic constraints, namely those referring to the surface activation process (initiation). It is known that these processes are difficult in some metallic phases reacting in aqueous phase. If leaching time was much higher than 0.5 h, leaching efficiencies would surely increase and the results would be closer to the equilibrium predictions values.

The effect of residence time on the leaching efficiency was evaluated in a series of experiments. Concerning the behaviour of the hydroxides, Fig. 8 shows that the leaching efficiency of Ni, Cd and Co increased with time even using low acid concentrations (pH 1–3) and ambient temperature. Consid-

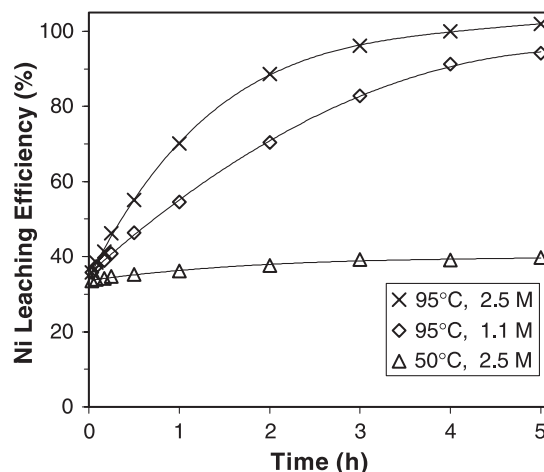


Fig. 9. Leaching efficiency of nickel as a function of time, at different conditions of temperature and  $\text{H}_2\text{SO}_4$  concentration;  $L/S = 17 \text{ L/kg}$ .

ering the leaching at pH 3, the solubilisation yields attained after 5 h of reaction were 17% for Ni, 64% for Cd and 54% for Co, while in previous tests carried out with 0.5 h, the values achieved were 1% for Ni, 12% for Cd and 5% for Co. Therefore it can be expected that experimental data could eventually fit well the predicted equilibrium calculations if long residence times were utilised.

The effect of time in the leaching efficiency of nickel contained in the electrode materials, for different values of temperature and acid concentration, can be observed in Fig. 9. The beginning of the leaching curves starts at about 33–35% of yield, which corre-

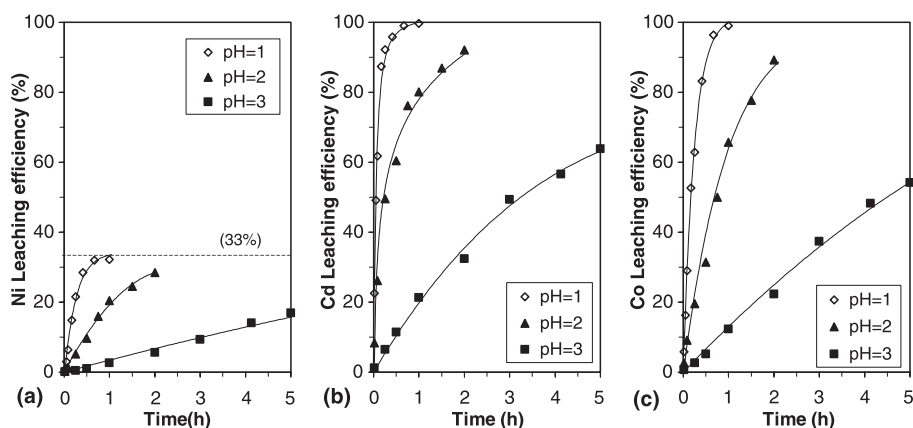


Fig. 8. Leaching efficiency of Ni, Cd and Co in low concentrated  $\text{H}_2\text{SO}_4$  solutions (pH 1, 2 and 3) as a function of time;  $T = 25^\circ\text{C}$ ;  $L/S = 20 \text{ L/kg}$ .

sponds to the complete dissolution of  $\text{Ni}(\text{OH})_2$  in the first minutes of reaction. This was expected due to the relatively high acidity levels. Values above 33% of yield are attributed to the reaction of nickel in metallic form ( $\text{Ni}^0$ ) as previously referred. Temperature plays an important role in the dissolution of  $\text{Ni}^0$ . At 50 °C the leaching efficiency is almost imperceptible while at higher temperatures the leaching is markedly improved. A residence time of 4 h is enough to achieve complete dissolution at 95 °C. The leaching efficiency decreases with low acid concentration such as 1.1 M, but the effect of concentration seems to be less relevant than temperature. However, in order to attain practical yields in an adequate time, it is recommended to use more aggressive conditions of temperature and acidity.

Results obtained for the other metals at the acidity levels tested in this study showed that, after 5 min of reaction, more than 95% of Co and Cd were solubilised and a complete dissolution was achieved after 10 min.

## 5. Conclusions

Sulphuric acid leaching, the first chemical step of an integrated process for recovering metals from spent Ni–Cd batteries, was tested. Hydroxide phases of Ni, Cd and Co present in electrode materials were readily soluble in a few minutes at room temperature at relatively low acid concentrations (e.g. pH ~ 1). The use of higher pH conditions markedly decreased the leaching efficiency. Nickel present as metallic phase was more resistant to leaching, requiring the use of high values of temperature and acid strength to achieve adequate conversions in reasonable time. This behaviour revealed a strong kinetic limitation since equilibrium calculations indicated that, at room temperature and below pH 4.5, the conversion of  $\text{Ni}^0$  into  $\text{Ni}^{2+}$  should occur spontaneously. However, it is known that practical leaching behaviour of some solid phases is quite different because physical, structural and often kinetic factors give rise to deviations from predicted values. The effect of temperature on the leaching efficiency of nickel is relevant, but for improving the leaching rate, the influence of acid concentration is also an important variable. For an acid concentration of 2.5 M  $\text{H}_2\text{SO}_4$ , L/S ratio of 17 L/kg and 95 °C temperature, the Ni metallic phase was totally leached after 4 h of reaction.

## Acknowledgements

The authors gratefully acknowledge the financial support made by Fundação para a Ciência e Tecnologia-Programa Praxis XXI.

## References

- Bärring, N.E., 1979. Recovery and treatment of process wastes at a nickel–cadmium battery factory in Sweden. Proceedings of the 2nd International Cadmium Conference, Cannes, February 6–8, 1979. Cadmium Association, London, pp. 105–106.
- Bärring, N.E., 1983. Recycling of nickel–cadmium batteries and process wastes—processes and operations of the new SAB NIFE plant. Proceedings of the 4th International Cadmium Conference, Munich, March, 1983. Cadmium Association, London, pp. 58–60.
- Cavallini, M., Lupi, C., Pilone, D., Milella, P.P., Pescetelli, A., Cannavale, G., 2000. Laboratory and pilot plant processing of spent Ni–Cd batteries. Recycling of Metals and Engineered Materials, Pittsburgh, Pennsylvania, October 22–25, 2000. TMS, Warrendale, Pennsylvania, pp. 471–478.
- Espinosa, D.C.R., Tenorio, J.A.S., 2001. The use of unit operations of mining treatment as the first step of Ni–Cd batteries recycling. EPD Congress 2001, New Orleans, Louisiana, February 11–15, 2001. TMS, Warrendale, Pennsylvania, pp. 173–181.
- Hanewald, R.H., 1998. The collection and processing of spent Ni–Cd batteries in North America and INMETCO's role. Battery Recycling '98, Proceedings of the 4th International Battery Recycling Congress, Hamburg, July 1–3, 1998.
- Linck, F., 1998. SNAM company update and recycling service. Battery Recycling '98, Proceedings of the 4th International Battery Recycling Congress, Hamburg, July 1–3, 1998.
- Nogueira, C.A., Delmas, F., 1999. New flowsheet for the recovery of cadmium, cobalt and nickel from spent Ni–Cd batteries by solvent extraction. *Hydrometallurgy* 52 (3), 267–287.
- Ohira, Y., 1986. Current status concerning the recycling of sealed nickel–cadmium batteries in Japan. Proceedings of the 5th International Cadmium Conference, San Francisco, February 4–6, 1986. Cadmium Association, London, pp. 41–44.
- Pons, C., Nogueira, C.A., Dalrymple, I., Rodrigues, F., Delmas, F., Margarido, F., Pena, M., 1997. Development of a hydrometallurgical process for the recycling of metals from nickel–cadmium batteries and other similar wastes. The Recycling of Metals, Proceedings of the third ASM International Conference and Exhibition, Barcelona, June 11–13, 1997. The Materials Information Society, Brussels, pp. 487–498.
- Pourbaix, M., 1974. Atlas of Electrochemical Equilibria in Aqueous Solutions, 2nd ed. NACE, Houston.
- Sohn, J.S., Park, K.H., Park, J.S., Jeon, H.S., 2000. Preparation of nickel sulfate from spent nickel–cadmium batteries. Recycling of Metals and Engineered Materials, Pittsburgh, Pennsylvania, October 22–25, 2000. TMS, Warrendale, Pennsylvania, pp. 479–486.